APPLICATION OF MIXTURE-THEORY FOR THE OPTIMISATION OF THE COMPOSITION OF THE NUTRIENT SOLUTION

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Abstract

This study demonstrates that nutrient solutions can be defined as 'mixture systems'. A general methodology for design and analysis of mixture optimisation experiments is developed. The emphasis is centred on multivariate investigation of the zone of optimal solution properties as a function of the ion composition and the total ionic concentration of the solution. The study of the effects of ion interaction on well defined solution properties is also possible by this multivariate approach. This work is a valuable tool in mineral nutritional research, because for the first time the chemical feasibility conditions of such solution, combined with additional chemical, physiological or economical constraints, form the foundation of the statistical experimental design theory, which makes the optimisation of complex mixtures of ions in relation to well-defined response variables possible.

1 Introduction

Nutrient solutions are very important both in daily practice and in scientific research. The last decade the need for production diversification and increase, led to a more intensive horticultural production in greenhouses with computerised control of the climate and the fertigation. All economically important horticultural products like tomatoes, lettuce, peppers, cucumbers, cutflowers, chicory and so on, are all grown with nutrient solutions. Nutrient solutions optimised for specific crop production contribute to the competitivity of horticultural production.

Also in many other fields like plant and animal tissue cultures and fermentation technology nutrient solutions are important.

In the past and even in today's scientific research many investigators have grown crops in nutrient solutions chosen largely at random. For nearly all crops special compositions of the nutrient solution, sometimes even more than 50 recipes for one crop can be found (Ebbinge Wubben, 1948; Steiner, 1972). Some of these formulae were even not chemically feasible in solution, because of the fact that the solubility products of some ion combinations were exceeded.

Optimising the nutrient solution means to describe the zone of the mineral composition of the nutrient solution that gives an optimal development, production and quality of the produce. Taking into account that systematic research into the impact of the mineral composition of the nutrient solution is only justified if one deals with the relative ratios of the ions (Steiner, 1961), different elements have to be changed at the same time. This can only be realised using a multivariate approach, making use of mixture theory. A supplementary advantage of the mixture theory is the necessity of only a limited number of experimental units to investigate a large experimental region, resulting in cheaper, faster and easier experimentation.

2. Material and methods

2.1. The nutrient solution

A nutrient solution can be considered as an aqueous solution of ions. The chemical composition of a nutrient solution is determined by the relative cation proportions, the relative anion proportions, the total ionic concentration and the pH (Steiner, 1961).

In general the nutrient solutions for plant production consist besides of the essential micro-elements (Fe, Mn, Zn, Cu, B, Cl and Mo) out of six essential macro-elements : three cations : K, Ca and Mg and three anions : N, P and S.

The fact that these ions can only be put in the solution by dissolving salts, imposes the major constraint on nutrient solutions namely : the sum of the cation equivalents must equal the sum of the anion equivalents. This ionic balance constraint is the major reason for the impossibility of classical orthogonal experimentation with nutrient solutions and the main argument to define nutrient solutions as mixture systems where the components can not be varied independently because the sum of the components must remain constant (Schrevens, 1988).

The anions and the cations in a nutrient solution can be expressed as proportions. These proportions must be nonnegative and if they are expressed as fractions they must sum to unity. In a q-component mixture, with x_i being the proportion of the i-th mixture component the following restrictions are to be considered :

$$0 \leq x_i \leq 1 \qquad \text{for } i = 1, 2, 3, ..., q \qquad (1)$$

$$\sum_{i=1}^{q} x_i = 1 \qquad (2)$$

The q components of the system (x_1 to x_q) are called "mixture variables". The restrictions (1) and (2) reduce the experimental factor space of q dimensions to a q-1 dimensional simplex, as described by Claringbold (1955). For the ionic balance constraint in nutrient solutions this renders :

$$[K^+] + [Ca^{2+}] + [Mg^{2+}] = [NO_3^-] + [H_2PO_4^-] + [SO_4^{2-}] = C/2$$

With C being the total ionic concentration in mval/l.

This gives for both the cation and the anion factorspace a three dimensional factorspace that can be represented in a two dimensional simplex. The representation of the proportions as single points in trilinear co-ordinates can be done by making the proportions correspond to the length of the perpendiculars from each verticex to the three sides of an equilateral triangle, each side representing the proportions of one of the three mixture variables.

Besides the ionic balance constraint different precipitation constraints have to be taken into account. The solubility products of ion combinations may not be exceeded. The interpretation of experiments involving such cases would therefore be seriously affected. Depending on the total ionic concentration used, these precipitation constraints further reduce the feasible experimental factorspace.

2.2. The experimental design

Considering the 6 essential macronutrients, the only calcium salt, with high solubility is calciumnitrate. This means that if all 6 essential macronutrients are to be used, experimentation over the whole simplex is not possible. Also physiological constraints do not allow experimentation over the whole simplex. Therefore a subregion needs to be taken out of the whole simplex, taking into account possible precipitation and dissociation reactions. If the experimental region is simplex shaped, it can be defined in terms of 'Pseudocomponents' (Kurotory, 1966; Crosier, 1984 and 1986). In this case designs used to explore the whole simplex, such as simplex lattice or simplex centroid designs can be used, when expressed in pseudocomponents (Schrevens and Cornell, 1993).

2.3. Cation experiment

On 18 March 1994 1.5 g English Ryegrass seed was sown on each polyurethane slab (10 cm x 10 cm and 0.5 cm high). Nine of these slabs were placed on a Grodan rockwool slab (1 m x 0.2 m and 0.075 m high). The rockwool slab was placed in a plastic Libra tray. The Libra trays were placed at random in a greenhouse with climate control. Each tray was fertigated with a different nutrient solution with a total ionic concentration of 25 mval/l.

A simplex lattice design extended with the overall centroid was setup in the cation factorspace (K^+, Ca^{2+} and Mg^{2+}) (Table 1 and Figure 1). Nutrient solution 1, 2 and 3 are the vertices of the simplex, solution 4, 5 and 6 are the edge centroids and solution 7 is the overall centroid. The concentration of each ion in each solution can easily be calculated by multiplying the proportion with the total concentration of cations (12.5 mval/l). The anion composition was the same for all the nutrient solutions and the same as combination 7 in the anion experiment (Table 1). The composition of the micronutrients is the same in all the nutrient solutions (Table 2)

On 8 April 1994, three weeks after sowing, the grass on 8 polyurethane slabs of each rockwool slab was harvested. After a multiple regression of the dependent variable (total fresh weight) in function of the mixture variables a second order canonical polynomial was obtained. This polynomial represents the response surface of the dependent variable in function of the composition of the mixture variables for the experimental region.

2.4. Anion experiment

For the anion experiment the Ryegrass was cultivated in exactly the same way and at the same time as in the cation experiment. A simplex lattice design extended with the overall centroid was setup in the anion factorspace (NO_3^-, $H_2PO_4^-$ and SO_4^{2-}) resulting in 7 nutrient solutions (Table 1 and Figure 2). The cation composition was the same for all nutrient solutions and is the same as solution 7 in the cation experiment (Table 1). The total ionic concentration of all the solutions is 25 mval/l. The composition of the micronutrients is the same as in the cation experiment (Table 2).

At the same time as for the cation experiment the grass on 8 polyurethane slabs was harvested. A multiple regression of the dependent variable in function of the mixture variables resulted in a second order canonical polynomial.

2.5. Double mixture experiment

A nutrient solution consists out of a mixture of cations and a mixture of anions. Therefore nutrient solutions can be considered as double mixtures. For this double mixture experiment each combination of cations in the cation experiment is combined with each combination of anions in the anion experiment (Table 1), resulting in 49 nutrient solutions. The composition of the micronutrients is the same for all nutrient solutions (Table 2). The Ryegrass is cultivated under the same circumstances and at the same time as in the cation experiment.

The model consists of the product of both the anion and the cation model.

3. Results

3.1. The cation experiment

The response surface for the production of Ryegrass in the experimental region of the cation experiment can be expressed with the following second order canonical polynomial (Figure 3) :

$$\text{production} = 1379.1*K - 34.6*Ca + 1606.8*Mg + 4193.0*K*Ca - 114.2*K*Mg + 1177.6*Ca*Mg \qquad (R^2=0.99)$$

with K, Ca en Mg in proportions

Considering the main effects, magnesium and potassium have the strongest impact on the production of Ryegrass. Calcium and potassium strongly interact synergetically for the production. The highest production is achieved if the proportion of magnesium in the solution is lowest (0.12 or 1.5 mval/l) and the proportion calcium is 0.28 (3.5 mval/l), so the proportion potassium has to be 0.6 (7.5 mval/l). Also calcium and magnesium interact synergetically, while there exists an antagonistic interaction between potassium and magnesium for the production.

3.2. The anion experiment

The response surface for the Ryegrass production in function of the anion composition of the nutrient solution (Figure 4) can be expressed with the next polynomial :

$$\text{production} = 2319.3*NO_3 + 2665.0*H_2PO_4 + 699.0*SO_4 - 6298.4*NO_3*H_2PO_4 - 1860.5*NO_3*SO_4 + 14743.9*H_2PO_4*SO_4 \qquad (R^2=0.98)$$

with NO_3, H_2PO_4 and SO_4 in proportions

The major positive main effects on production are caused by dihydrogenphosphate and nitrate. If the proportion sulphate in the nutrient solution is low, the nitrate proportion has a positive influence on production. Increasing the sulphate proportion, turns the positive effect of the nitrate proportion into a negative effect. This is caused by the antagonistic interaction for the production between nitrate and dihydrogenophosphate and between nitrate and sulphate. Sulphate and dihydrogenophosphate strongly synergetically interact for the production. The highest production is achieved when a low proportion nitrate is used (0.56 or 7 mval/l), a proportion sulphate of 0.24 (3 mval/l) and a proportion dihydrogenophosphate of 0.20 (2.5 mval/l).

3.3. The double mixture experiment

For each specific cation composition (Table 1) a different anion composition with optimal production can be found (Figure 5). The highest production can be found for a low potassium proportion and increases if at a low potassium proportion the magnesium proportion increases or the proportion calcium decreases. A nutrient solution with cation composition 3 (Table 1) renders the highest production for a proportion nitrate, dihydrogenophosphate and sulphate of respectively 0.56, 0.36 and 0.09. For a high potassium proportion, the lowest production can be found at a high sulphate and a low nitrate concentration. If a high calcium proportion is present in the nutrient solution, a low sulphate and a low nitrate (or a high dihydrogenophosphate proportion) renders the lowest production. The presence of a high magnesium proportion in the solution renders the lowest production if the solution contains a low proportion sulphate and a high proportion nitrate.

For each specific anion composition (Table 1) a different cation composition can be found with an optimal response for the dependent variable (Figure 6). The production of Ryegrass increases if the proportion nitrate in the nutrient solution decreases. At a low nitrate proportion, the production increases if the proportion dihydrogenophosphate decreases and the proportion sulphate increases. Sulphate is the most beneficial ion, if a high production is intended. The anion combination 3 (Table 1) renders the highest production for a potassium, calcium and magnesium proportion of respectively 0.44, 0.20 and 0.36. The same anion composition renders the lowest production with the same potassium proportion, a calcium proportion of 0.44 and a magnesium proportion of 0.12. The strong negative effect of the magnesium proportion on the production decreases if the dihydrogenophosphate proportion in the solution decreases.

4. Conclusions

Nutrient solutions can be considered as mixture systems. Systematic research into the optimisation of nutrient solutions, is only justified if the relative proportions of the different ions are considered. This necessitates for a multivariate approach, using mixture theory.

Using mixture designs it is possible to investigate a large experimental region with only a limited number of nutrient solutions, by use of optimal design theory.

According to the specific cation or anion combination used to investigate the experimental region in the respectively anion or cation factorspace, a different optimal composition of the anions respectively cations can be found.

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Tabel 1 : Composition of the nutrient solutions expressed as proportions in mval/l

Cation experiment				Anion experiment			
Solution number	K^+	Ca^{2+}	Mg^{2+}	Solution number	NO_3^-	$H_2PO_4^-$	SO_4^{2-}
1	0.44	0.44	0.12	1	0.82	0.09	0.09
2	0.79	0.09	0.12	2	0.56	0.35	0.09
3	0.44	0.09	0.47	3	0.56	0.09	0.35
4	0.615	0.265	0.12	4	0.69	0.22	0.09
5	0.615	0.09	0.295	5	0.56	0.22	0.22
6	0.44	0.295	0.265	6	0.69	0.09	0.22
7	0.556	0.207	0.237	7	0.65	0.175	0.175

Tabel 2 : Addition of the micro-nutrients in the nutrient solutions

Salt	Micromol/l of salt
$ZnSO_4.7H_2O$	0.9375
$CuSO_4.5H_2O$	0.3125
$MnSO_4.H_2O$	21.875
H_3BO_3	15.875
$(NH_4)_6Mo_7O_{24}.4H_2O$	0.045
FeHEEDTA 4.5 %	63.5

{3,2} Simplex centroid design

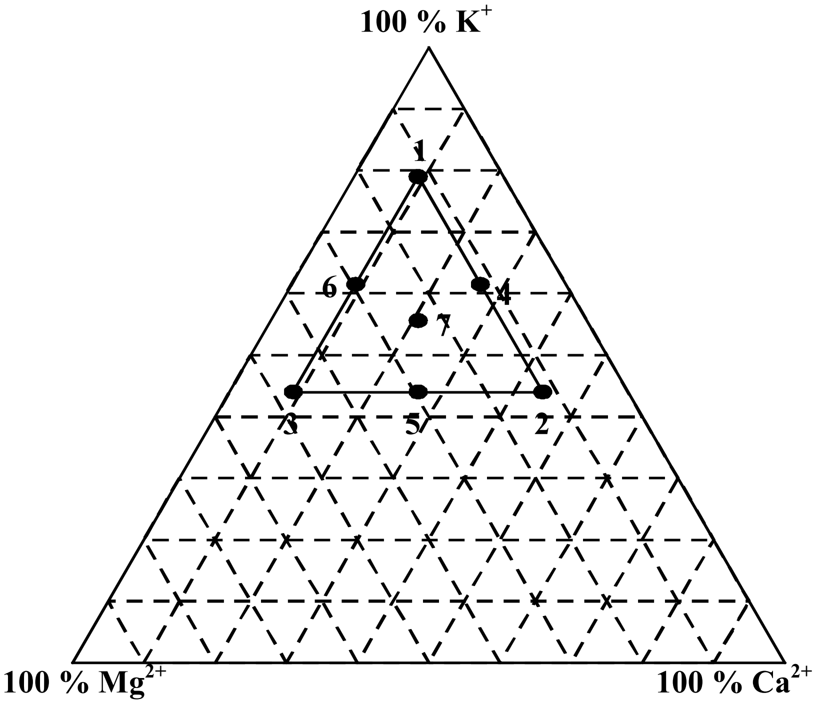

Fig 1 : Experimental region for the cation experiment

{3,2} Simplex centroid design

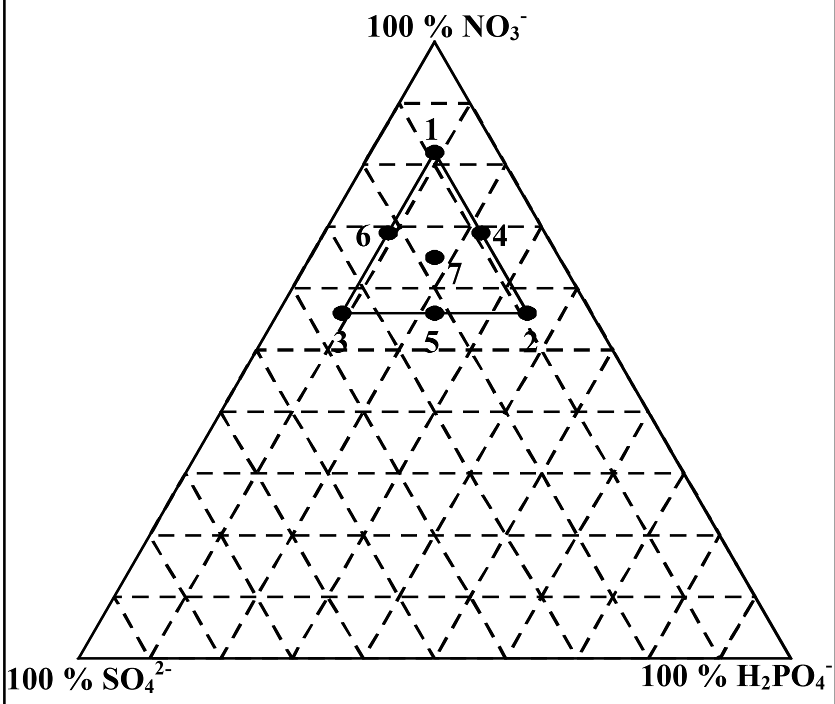

Fig 2 : Experimental region for the anion experiment

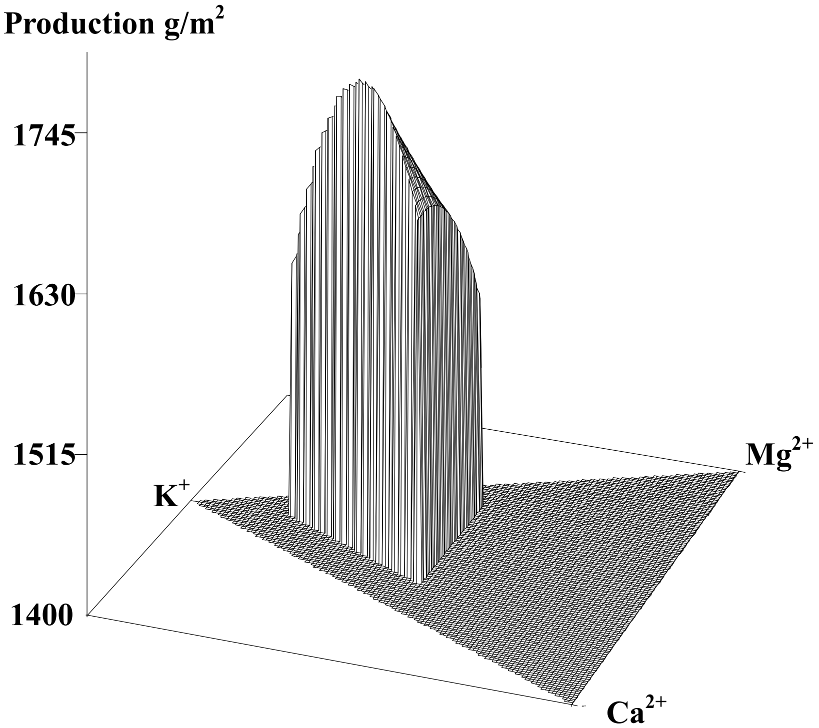

Fig 3 : Ryegrass production in function of the cation composition

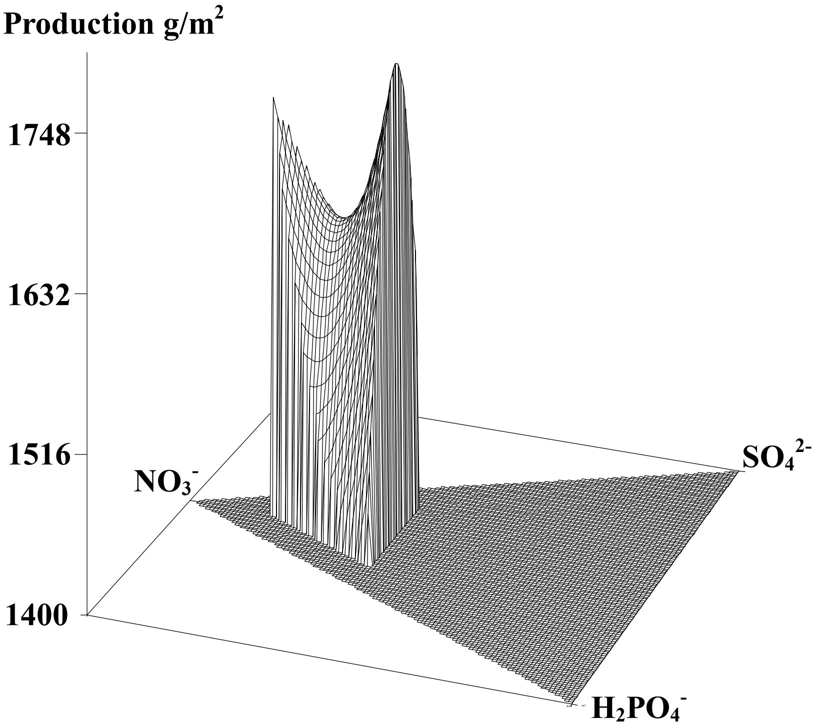

Fig 4 : Ryegrass production in function of the anion composition